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# Review on analysis of biodiesel with infrared spectroscopy

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ABSTRACT

Biodiesel is primarily obtained from the base catalyzed transesterification reaction of oils or fats. Biodiesel has become more attractive due to its characteristics of being bio-degradable, renewable and non-toxic. Recently biodiesel has been widely used as an alternative fuel. Biodiesel quality analysis has become very important because consistency and a higher quality are paramount to the success of its commercialization and market acceptance. Suitable and precise analytical methods are needed to meet this requirement. Some analytical techniques have been considered and applied in biodiesel analysis, such as Chromatography and Spectroscopy. Within the Spectroscopic technique, Infrared Spectroscopy has played an important role. Past reviews on analytical methods for biodiesel analysis were written by Knothe and Marcos Roberto Monteiro. In this paper, the author has discussed the developments in biodiesel quality analysis with IR technique.



**Contents**



## 1. Introduction

A majority of the world's energy needs are supplied through petroleum fuels which are finite and will be consumed shortly at current usage rates [1]. The energy crisis has directed scientists to search for renewable alternative fuels. Another important reason for the research on alternative fuels is that petroleum fuel has pollutant and hazardous effects on the environment. The usable alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. Biodiesel has many advantages when compared with conventional diesel fuel. The advantages of biodiesel are its portability, availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number, and higher biodegradability [2]. The most important advantages of biodiesel are its renewability and biodegradability. Biodiesel can be recycled by nature, or can be broken down into its smallest parts through the actions of microorganisms, so that it will not pollute the environment. Moreover, the reduction of exhaust emissions, due to its minimal amounts of sulfur, carbon dioxide, and aromatic content, make biodiesel an environmentally friendly fuel [3,4].

Biodiesel is produced by transesterification in which, oil or fat reacts with a monohydric alcohol in the presence of a catalyst. During the reaction process, intermediate glycerols, mono- and diacylglycerols, are formed; small amounts of which might remain in the final biodiesel product. In addition to these partial

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**Nomenclature**

| | |
|---|---|
| ANN | Artificial Neural Network |
| ATR | Attenuated Total Reflectance |
| ATR-FTIR | Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy |
| DF | diesel fuel |
| DRIFTS | Diffused Reflectance IR Fourier Transform Spectra |
| DTGS | Deuterated Triglycine Sulfate Detector |
| EFCM | Enterprise Fabric Connectivity Manager |
| FA | fatty acid |
| FAEE | fatty acid ethyl esters |
| FAME | fatty acids methyl esters |
| Far-IR | Far Infrared Spectroscopy |
| FFA | free fatty acids |
| FPME | field pennycress methyl esters |
| FTIR | Fourier Transform Infrared Spectroscopy |
| FT-MIR | Fourier Transform middle Infrared Spectroscopy |
| FT-NIR | Fourier Transform near Infrared Spectroscopy |
| GC | Gas Chromatography |
| GC–FID | Gas Chromatography–Flame Ionization Detector |
| H NMR | Hydrogen Nuclear Magnetic Resonance |
| HPLC | High-Performance Liquid Chromatography |
| H-PLS | Hierarchical Partial Least Square Regression |
| IR | Infrared Spectroscopy |
| KOH | potassium hydroxide |
| LC–GC | Liquid Chromatography–Gas Chromatography |
| ME | methyl esters |
| mid-IR | Middle Infrared Spectroscopy |
| MLR | Multiple Linear Regression |
| near-IR | Near Infrared Spectroscopy |
| PCA | Principal Component Analysis |
| PCR | Principal Component Regression |
| PLS | Partial Least Square Regression |
| PUFA | polyunsaturated fatty acids |
| RME | rape methyl esters |
| RMSE | root mean square error |
| RMSEP | root mean square error of prediction |
| RMSPD | root mean square prediction difference |
| S-PLS | Serial Partial Least Square Regression |
| TG | triacylglycerides |
| UFO | used frying oil |
| UV–vis spectroscopy | Ultraviolet and Visible Spectroscopy |
| VFA | Variable Filter Array |

glycerols, unreacted triacylglycerols as well as unseparated glycerol, free fatty acids (FFA), residual alcohol, and catalysts might contaminate the final product. Such contaminants will lead to severe operational problems when using biodiesel including engine deposits, filter clogging, or fuel deterioration. Therefore, standards are established such as EN 14214 used in Europe and ASTM D6751 in the United States. Besides these composition and purity parameters, the parameters used to define the property of biodiesel such as density, and viscosity are also described in these standards, which are described in Table 1. The main purpose of these standards is to guarantee the fuel quality and performance during practical application. Different feedstock for biodiesel production, different production process, and the subsequent handling methods all can influence biodiesel quality. Therefore, the assurance of fuel quality and properties is an issue of great importance to the successful commercialization of biodiesel.

In the last ten years, the quality control of biodiesel drew a great deal of attentions of many researchers. The important research issues related to several aspects. First, the determination of chemical composition and physical properties of biodiesel is

**Table 1**
Biodiesel standard.

| Property | ASTM D 6751 | | EN 14214 | |
|---|---|---|---|---|
| | Test method | Limits | Test method | Limits |
| Ester content | – | – | EN 14103 | 96.5% (mol/mol)min |
| Linolenic acid content | – | – | EN 14103 | 12.0% (mol/mol)max |
| Content of FAME with $\geq 4$ double bonds | – | – | – | 1.0% (mol/mol)max |
| MAG content | – | – | EN 14105 | 0.80% (mol/mol)max |
| DAG content | – | – | EN 14105 | 0.20% (mol/mol)max |
| TAG content | – | – | EN 14105 | 0.20% (mol/mol)max |
| Free glycerin | D 6584 | 0.020% (w/w)max | EN 14105 | 0.020% (mol/mol)max |
| Total glycerin | D 6584 | 0.240% (w/w)max | EN 14105 | 0.25% (mol/mol)max |
| Water and sediment | D 2709 | 0.050% (v/v)max | EN ISO 12937 | 500 mg kg$^{-1}$ max |
| Methanol content | – | – | EN 14110 | 0.20% (mol/mol)max |
| (Na+K) content | UOP 391 | 5.0 mg kg$^{-1}$ max | EN 14108 | 5.0 mg kg$^{-1}$ max |
| (Ca+Mg) content | – | – | PrEN 14538 | 5.0 mg kg$^{-1}$ max |
| P content | D 4951 | 0.001% (w/w)max | EN 14107 | 10.0 mg kg$^{-1}$ max |
| Oxidative stability (110 °C) | – | – | EN 14112 | 6 h min |
| Density(15 °C) | – | – | EN ISO 3675 | 860–900 kg m$^{-3}$ |
| Kinematic viscosity (40 °C) | D 445 | 1.9–6.0 mm$^2$ s$^{-1}$ | EN ISO 3104 | 3.5–5.0 mm$^2$ s$^{-1}$ |
| Flash point | D 93 | 130 °C min | EN ISO 3679 | 120 °C min |
| Cloud point | D 2500 | Not specified | – | – |
| Sulphur content | D 5453 | 0.05% (w/w) max | EN ISO 20864 | 10.0 mg kg$^{-1}$ max |
| Carbon residue | D 4530 | 0.050% (w/w)max | EN ISO 10370 | 0.30% (mol/mol)max |
| Cetane number | D 613 | 47 min | EN ISO 5165 | 51 min |
| Sulphated ash | D 874 | 0.020% (w/w)max | ISO 3987 | 0.02% (mol/mol)max |
| Total contamination | – | – | EN 12662 | 24 mg kg$^{-1}$ max |
| Copper strip corrosion (3 h, 50 °C) | D 130 | No. 3 max | EN ISO 2160 | 1 (degree of corrosion) |
| Acid number or acid value | D 664 | 0.50 mgKOH/g max | EN 14104 | 0.50 mg KOH/g max |
| Iodine value | – | – | EN 14111 | 120 g $I_2$/100 g max |
| Distillation temperature (90% recovered) | D 1160 | 360 °C | – | – |

the most important part of biodiesel quality analysis. It is worth noting that biodiesel is the product of the transesterification process, the reaction process has great effect on the final production, so it is important to monitor the reaction process in order to recognize, and correct problems at an early stage [5]. As mentioned above, the mono- and diacylglycerols, unreacted triacylglycerols, unseparated glycerol, free fatty acids, residual alcohol, and the catalyst might contaminate the final product. These contaminants can cause severe operational problems, thus the analysis of contaminants is a critical issue of biodiesel quality control. Meanwhile, illegal adulteration of biodiesel has been found, which also can cause some operational problems. The analytical methods to verify and determine the adulteration are very important. Additionally, the determination of blend levels is a key point of biodiesel analyses [5]. Moreover, the greatest problem of biodiesel currently is its high cost, which is mainly dependent on the feedstock being used. Nowadays, most biodiesel is made from high cost edible oils, thus finding other suitable low cost feedstock is another important issue. The feedstock used has obvious effect on the biodiesel quality, thus the feedstock selection and analysis are very important.

The ideal analytical method for biodiesel quality control would be able to reliably and inexpensively quantify all contaminants even at trace levels with experimental ease in seconds or even faster for on-line reaction monitoring [6]. Various analytical methods were tried for analyzing the contaminants, blend level, and adulteration, or for monitoring the transesterification process and other analytical needs stated earlier. Unfortunately, no current analytical method meets these extreme demands. Among these methods, the commonly used analytical methods for analyzing biodiesel are chromatography and spectroscopy. Gas Chromatography (GC) has to be the most widely used method for the biodiesel analysis due to its generally higher accuracy in quantifying minor components. Another one named high-performance liquid chromatography (HPLC) is used commonly as well. However, biodiesel analyses with GC are very expensive and time consuming. Infrared Spectroscopy (IR) is a well established alternative nondestructive analytical technique which allows reliable, direct, and fast determination of several properties without sample pretreatment. Recently discovered as a cheaper and faster analytical method, IR has been widely applied in almost every aspect of biodiesel quality control. Therefore, the objective of this paper is to describe the application of IR in the accomplishment of biodiesel quality analysis.

Previously, reviews on analytical methods used for biodiesel analysis were published by Knothe and Monteiro, etc. [5–7] which showed the main analytical techniques developed prior to 2008.

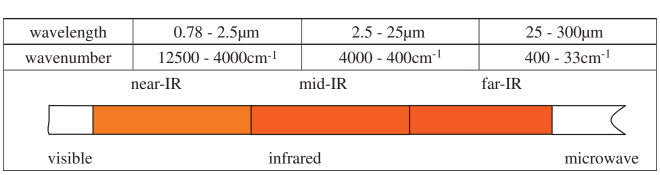



**Fig. 1.** The spectrum ranges of IR.

In this paper, the author tried to make an updated review focusing on biodiesel analysis with the IR technique. The research work focused primarily on the reported achievements of biodiesel analysis with the IR technique, including near infrared spectroscopy (near-IR) and middle infrared spectroscopy (mid-IR).

## 2. General introduction on infrared spectroscopy

The infrared spectroscopy (IR) technique refers to energy in the region of the electromagnetic radiation spectrum at wavelengths longer than those of visible light but shorter than those of radio waves. IR region covers a wide range of the electromagnetic spectrum, which is divided into three areas in order to provide the requirements of instruments for their different applications [8]. These areas are defined as near infrared (near-IR), middle infrared (mid-IR), and far infrared (far-IR). Fig. 1 shows the wavelength and wave number ranges of these IR regions. A basic introduction concerning near-IR and mid-IR is given in the following, but far-IR is not the focus here.

Mid-IR represents the spectrum of absorption of all the chemical bonds, such as O–H, N–H, C=O, C–H and so on. The spectrum is sensitive to the physical and chemical states of individual constituents in a sample between 4000 and 400 $cm^{-1}$. The most common use of mid-IR is to determine the chemical functional groups in the sample since different functional groups absorb characteristic frequencies of infrared radiation. Fig. 2 illustrates the absorptions of functional groups in the mid-IR region.

Currently, mid-IR spectroscopy is widely used for biodiesel analysis due to the higher incidence-spectral bands in this region as well as the higher intensity and specificity of the signal. The region between 1500 and 800 $cm^{-1}$ in mid-IR region was named the fingerprint region [9] where the absorptions included the contributions from complex interacting vibrations which gave each compound the unique information. Mid-IR is also used for both qualitative and quantitative analysis in analytical chemistry. Substances in very low concentrations are difficult to determine because the noise level in this region can cause problems. The development of the Fourier transform technique has greatly improved the development and application of IR techniques by improving the quality of infrared spectra and minimizing the time required to obtain data. After combined with the Fourier transform technique, IR played a more important role in analytical work.

The near-IR spectrum is composed of a combination of tones and overtones of fundamental vibrations of the functional groups, such as NH, OH, and CH groups. Near-IR is more useful for quantitative analysis of complex mixtures that contain these kinds of functional groups. Stretching and bending are two main types of molecular vibrations that describe the different molecular vibrational motion. Bending is defined as the change in the bond's angle that can be rock or deformation depending on if the movement is in the same or opposite directions. Stretching can be symmetrical when it is in the plane or asymmetrical when it is out of the plane. The help of computers and chemometrics will be needed during this kind of analytical work. Since the molecular

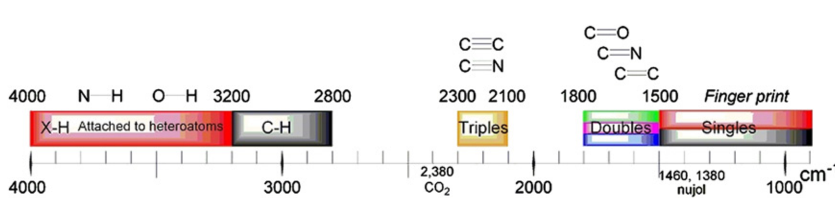



**Fig. 2.** The absorptions of the functional groups in mid-IR region.

structure of most compounds is very complex, the resulting spectra will have many overlapping peaks and valleys, therefore a statistical method will be required to identify specific features from these spectra. Near-IR has also gained increased interest in the process control of applications [10]. Near-IR has many advantages over other vibrational spectroscopic techniques and classical methods, such as being non-destructive, high-speed, and little or no sample preparation. In addition, near-IR spectroscopy provides a low cost instrumentation with a high signal-to-noise ratio [11,12]. Besides these advantages, the possibility of simultaneous determination of several quality parameters is worth mentioning, which means several parameters can be extracted simultaneously from the single spectra with multivariate analysis methods. Near-IR also suffers from a number of disadvantages; namely, the low sensitivity of the signal while compared with mid-IR, in which low concentration components cannot expect to be determined by the use of near-IR. Another disadvantage is the superposition of many different overtone and combination bands, which cause a very low structural selectivity, while in mid-IR region, many fundamentals can usually be observed in isolated positions. These overlapping signals also give rise to a spectrum with broad peaks, making the spectra very difficult to interpret.

IR can be used for analyzing almost all kinds of samples. Liquids, solutions, pastes, powders, films, fibers, gases and surfaces can all be examined by IR spectroscopy [13]. Recently, IR has been commonly used as a useful tool in biodiesel analysis. Certainly the traditional analysis methods for biodiesel are slow, costly, time consuming, require highly skilled operators, and are not easily adapted to on-line monitoring. The enormous developments in spectroscopy have provided the chance to obtain both quantitative and qualitative information about a sample of interest in a more straightforward and painless way. Fig. 3 shows the IR spectra of biodiesel and diesel samples. Fig. 3a shows the mid-IR spectra and Fig. 3b shows the spectra in near-IR region. Obvious different absorptions between the spectra of biodiesel and diesel can be observed in Fig. 3. Moreover, different kinds of biodiesel and various biodiesel concentrations in biodiesel–diesel blends are displayed in the different absorptions in the IR spectra. That is the reason why IR can be used in identifying and quantifying biodiesels in biodiesel quality control.

## 3. Application of IR technique on biodiesel analysis

### 3.1. Biodiesel feedstock selecting

In general, biodiesel feedstock can be categorized into three groups: vegetable oils (edible or non-edible oils), animal fats, and used waste cooking oil. Feedstock is very important for biodiesel production as the cost of biodiesel is greatly influenced by the feedstock being used. Presently, feedstock acquisition accounts for at least 80% of the costs associated with biodiesel production [14,15]. High feedstock cost is a serious economic disadvantage of biodiesel. Meanwhile the final properties of the biodiesel are affected greatly by the qualities of the iodine value, the water content and the free fatty acid content of the feedstock. Thus the feedstock used for biodiesel producing is needed to be analyzed and controlled.

Among the methods used for low cost feedstock selection and properties analysis, the mid-IR technique plays an important role. The most common use of mid-IR in feedstock analysis is free fatty acid (FFA) determination, since FFA content is a critical parameter in the conversion of oils to methyl esters [16–19]. The first research related to this subject is reported by Özgül-Yücel and Proctor [16]. The author proved that high-FFA rice bran, which cannot be used for producing good quality food oil, would be a fine feedstock for biodiesel production. Instead of using extraction and the subsequent titration method, the Fourier Transform Infrared (FTIR) spectroscopic method was used to rapidly measure rice bran FFA. The diffused reflectance IR Fourier transform spectra (DRIFTS) of the bran were obtained. The most significant spectral changes were in the carbonyl region (1760–1700 $cm^{-1}$) due to the acylglyceride carbonyl peak (1743 $cm^{-1}$) which decreased and the FFA carbonyl peak (1712 $cm^{-1}$) which increased. Calibration models were established by using the entire mid-IR spectrum (4000–400 $cm^{-1}$) and carbonyl region (1731–1631 $cm^{-1}$). When the calibration models were used for validation test, the correlation coefficient obtained were 0.96 and 0.88, the root mean square error (RMSE) were 3.64 and 5.80, respectively. This research work indicated FTIR can be used as a useful tool for measuring the FFA level of rice bran prepared for biodiesel production.

Other similar research works have been recently reported. A NaHNCN-based FTIR FFA method to determine FFA content in oils destined for biodiesel production was pointed out by Aryee et al. [17]. The feedstock which was analyzed consisted of fish oils extracted from salmon skin which is a fish tissue, typically considered useless and thus commonly discarded. There exists high polyunsaturated fatty acids (PUFA) in the fish tissue which is extremely prone to both lipolysis and oxidation, thus the oils extracted from this fish tissue tend to have high levels of free fatty acids (FFAs). Such FFAs are problematic during the conversion of oils to methyl esters for biodiesel in case the transesterification reaction is carried out in methanol with alkaline catalysis. The carboxylate absorbance at 1573 $cm^{-1}$ in the spectrum of the methanol phase was measured to determine the FFA content and

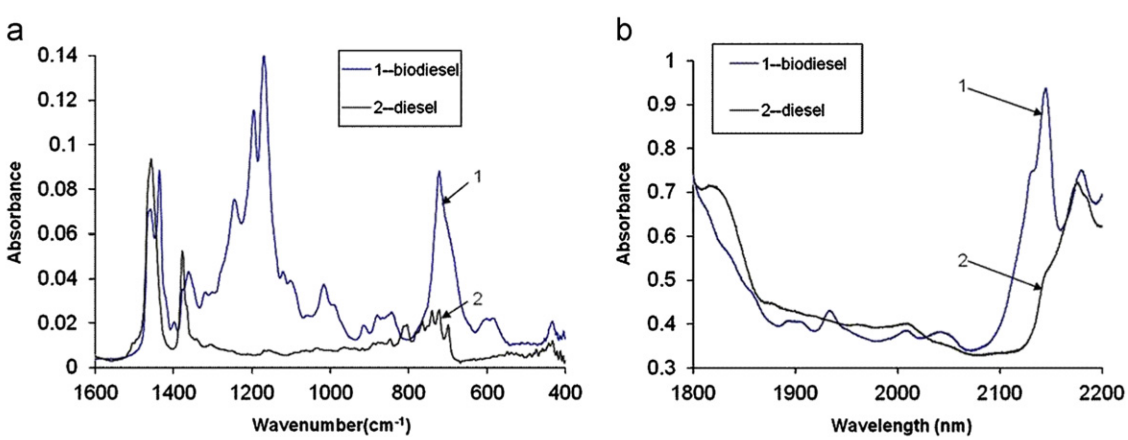



**Fig. 3.** IR spectra of biodiesel and diesel. (a) The mid-IR spectra and (b) The spectra in near-IR region.

the FTIR analytical results were compared with the results obtained by the titrimetric method. The researchers concluded that both methods responded in a comparable manner and the FTIR method was more reproducible and accurate as well as easier to carry out. By using the same FTIR method on a low-resolution IR spectrometer, a portable variable filter array (VFA) IR spectrometer, the FFA of edible oils was determined and the research result was reported in Ref. [18].

Another common use of FTIR in feedstock analysis for biodiesel production is to try to make sure some kind of low cost feedstock is suitable for biodiesel production. Field pennycress oil was analyzed by Moser et al. [19]. After the transesterification of field pennycress oil, the FTIR spectra of field pennycress methyl esters (FPME) were obtained on a Thermo-Nicolet Nexus 470 FTIR spectrometer in a scanning range of 650–4000 $cm^{-1}$. The spectra of FPME were found to be qualitatively similar to spectra of fatty acids methyl esters (FAME) reported before. For example, FPME contained a methyl ester moiety that was prominently indicated in the FTIR spectrum by a strong carbonyl signal of 1742 $cm^{-1}$. This research work indicates that FTIR is useful in biodiesel feedstock analysis due to the functional group information provided in this region. Similar research work was reported by Jham et al. [20], Sarin et al. [21], Shang et al. [22], and Qin et al. [23]. In these research works, wild mustard (*Brassica juncea* L.) oil, *Guizotia abyssinic* oil, *Pistacia chinensis* oil and Tung oil were analyzed for the possibility of being used for biodiesel production with the method of comparing the FTIR spectra of the corresponding methyl esters obtained with the known FTIR spectra of FAME. The results of the studies confirmed FTIR can be used to verify the possibility of utilizing these oils for biodiesel production as a potential alternative feedstock. Another possible biodiesel feedstock, Annona seed oil, was studied by Branco et al. [24] with FTIR, which resulted in a new use of FTIR technique. The FTIR spectrum of the recently extracted oil was registered in the entire mid-IR range of 4000 to 600 $cm^{-1}$. The FTIR spectra were registered every 24 h. The FTIR spectra of the Annona seed oil initially, after 8 days, and then 12 days under oxidative conditions showed some changes that could be used to indicate the oxidative process. Known from Branco's research, FTIR methods can be a useful tool for the evaluation and monitoring of the oxidation processes of the conversion of oil to biodiesel, to replace costly labor and time consuming chemical methods. Due to its lower cost, used frying oil is another promising alternative to vegetable oil for biodiesel production. Kleinová and Cvengroš [25] pointed out FTIR can be a useful tool for analyzing the characteristics of used frying oil (UFO) which could decide the properties of produced FAME. The detailed method was not given in this paper, but in the research work reported by Innawong et al. [26] this information can be found. In this work, FTIR spectra of fresh oil, used oil, and discarded oil in the entire mid-IR region were obtained. The fundamental and characteristic bands were further compared and analyzed with the principal component analysis (PCA) method to evaluate the quality of UFO. It is worth noting that in the research work stated above, mid-IR (FTIR) was preferred by the researchers in biodiesel feedstock analysis. The reason is that the spectra in mid-IR region consisted of fundamental and characteristic bands whose frequencies and intensities were clearly used for determining the functional groups in analyzed samples. The researcher discovered that besides the FTIR technique, other analytical methods such as GC were used together for analyzing work which meant further research should be investigated to more effectively utilize this potential analyzing tool. Recently, Baptista et al. [27] gave a fine example in better utilization of the IR technique in biodiesel feedstock analysis. In Baptista's research work, near-IR spectroscopy was used while several important oil properties such as the iodine value, the water content and the acid number were quantitatively analyzed with the IR technique. Meanwhile, the weight–weight percentages of different oil in mixtures were determined. Due to the development of computer technology and chemometrics, the advantage of multi-component analysis of near-IR can be fully utilized. Four different sets of samples were prepared and the near-IR diffused transmittance spectra of the oil samples were acquired and analyzed with multivariate methods of PCA, then calibration models were developed with partial least square regression (PLS). The performance of the calibration models was evaluated and the final results were determined to be acceptable.

### 3.2. Transesterification reaction monitoring

It is known that biodiesel is the final product of transesterification reaction of vegetable oils and animal fats with an alcohol, usually methanol, in presence of a catalyst, usually a base, such as KOH. Glycerol is a byproduct of the reaction. Partial transesterification products (mono- and diacylglycerols formed during the transesterification process), unreacted triacylglycerols, unseparated glycerol, free fatty acids, residual alcohol, and catalyst can contaminate the final product [28]. Therefore, it is important to be able to measure the yield of biodiesel accurately and to identify and quantify the various reaction components and by-products during the course of the reaction. In other words, the reaction must be monitored and controlled with proper analytical methods to ensure good biodiesel yield and quality production. It is also desirable that the analytical method be quick and easy to use. Many analytical methods have been used for the study of biodiesel transesterification such as GC and liquid chromatography–gas chromatography (LC–GC) and so on. However, despite their high accuracy, these methods are time consuming and cannot be easily used for the in situ evaluation of fast reversible reactions such as transesterification. IR technique has been used as a fast and accurate method to monitor the transesterification reaction process because of the chief advantages of accuracy, reliability, operational ease, rapidity of measurement, and nondestructive nature.

To the best of the author's knowledge, near-IR spectroscopy was first used in monitoring the transesterification reaction process for biodiesel production by Knothe [29,30]. In his work [29], near-IR spectra were obtained with a Perkin-Elmer Spectrum 2000 equipped with a Galileo transmission-type fiber-optic probe which made use of near-IR spectroscopy particularly easy. Knothe pointed out that while the mid-range infrared spectra of triacylglycerides (vegetable oils) and their corresponding methyl esters were very similar, the near-IR spectra of triacylglycerides (soybean oil used) and the corresponding methyl esters (methyl soyate) revealed two distinct possibilities for distinguishing them, one at 4425–4430 $cm^{-1}$, and the other at 6005 $cm^{-1}$. In both regions, the methyl ester displayed peaks while the triacylglyceride exhibited shoulders. Both peak regions were used for quantitative analysis. PLS approach was adopted for establishing the calibration model. Meanwhile, the biodiesel fuel quality was assessed with near-IR spectroscopy. The research work was extended and the fiber optic near-IR was used to monitor the transesterification process in progress [30]. Besides near-IR, another analytical method, H NMR spectroscopy was used for result correlating and cross-checking. This research work indicated the near-IR method could be used for monitoring the progress and endpoint of the transesterification reaction of biodiesel production. It is important to know that the near-IR spectra were primarily the results of many overlapped overtones and combination bands, which make the spectra complex and not directly interpretable. Furthermore, the sensitivities of near-IR were not as good as those of mid-IR region, which meant the

lower content (less than 0.1%) would be difficult to be quantified with near-IR. Mid-IR range of 4000 to 1500 $cm^{-1}$ was typical with many fundamentals with which the information of functional groups could be identified. Along with the recent advances in IR spectroscopy and signal transmission, several reports have been found using mid-IR to monitor the biodiesel production.

ATR-FTIR technology was used by Dubé et al. [31] to monitor the transesterification reaction based on the absorbance of characteristic functional groups in the lipid products. The conversion of TG to FAME involves the loss of the glycerol moiety, resulting in a decrease in peak height at 1378 $cm^{-1}$. The conversion of oil to FAME at time *t* can thus be defined by this decrease in peak height during the reaction. Instead of establishing a calibration model, an equation was given to calculate the conversion in the transesterification samples and the research result indicated that ATR-FTIR spectroscopy was a reliable conversion of oil to FAME data in a very short amount of time. In general, mid-infrared spectroscopy cannot be easily applied to analyze complex mixtures because peak overlapping usually compromises the spectral resolution. To overcome this problem, the multivariate analysis and the methods for the rapid acquisition of multi-signal spectra were used to explore the entirety of the analytically relevant information found in FTIR. Together with multivariate analysis methods, FTIR was successfully used in monitoring biodiesel production by other researchers. Zagonel, et al. [32] tried to monitor the transesterification kinetics of degummed soybean oil with FTIR and the multivariate approach. First, the entire FTIR spectral range of prepared samples was analyzed with the PCA method, the region with the greatest spectral differentiation was then identified. The final selected region with small differences was between 1700 and 1800 $cm^{-1}$ which included the stretching vibrations of carbonyl groups. Based on spectral data, the multivariate calibration model was then developed with the PLS regression. The model was evaluated and only small discrepancies were observed. Thus, the FTIR/PLS calibration model obtained was proved useful to predict changes in triolein-to-ester ratios and FTIR could be used as a simple and rapid analytical tool to determine the reaction yield of processes, such as the ethanolysis of vegetable oils.

Siatis et al. [33] used an FTIR methodology to determine the percentage of FAME in the n-hexane layer of the reaction. The new feedstock, seed cake, was used for the biodiesel production with the ultrasonically assisted extraction transesterification method. In order to determine the degree of conversion of TG to FAME, the samples with known concentrations of TG and FAME were prepared, then the spectra in the region from 1300 to 1060 $cm^{-1}$ was used to establish the calibration model with the PLS algorithm. Based on the model obtained, the various stages of the transesterification were monitored and the percentage of FAME in the TG/FAME mixture could be quantitatively and simultaneously determined. This work indicated the FTIR can be used for in situ monitoring. The seed cakes also have been proved to be a new feedstock for biodiesel production. Two years later, an online monitoring of the transesterification reaction was realized with ATR-FTIR and multivariate approach by Trevisan et al. [34]. Range 3707 to 814 $cm^{-1}$ in mid-IR was preferred due to more chemical information provided. Meanwhile multivariate analysis was used together because of the intense absorption overlapping. A cylindrical internal reflectance cell for liquid evaluation with a PbSe rod crystal was used to obtain the IR spectra through the infrared online monitoring process. Each spectrum was obtained in 15 s and the monitoring was carried out for 12 min. Four batches were carried out and for each monitored batch the spectrum data matrix was obtained and analyzed. The multivariate calibration models for determining the concentration of FAEE were developed with PLS and used to monitor the reaction process. Through the value of root mean square error of prediction (RMSEP) and root mean square prediction difference (RMSPD) obtained during the models comparison, ATR-FTIR has been proved to be a rapid and low cost method with potential to be used in process monitoring and reaction optimization. Later, the robustness of FTIR method was illuminated by Mahamuni and Adewuyi [35]. ATR-FTIR was used for the first time to monitor the transesterification reaction to determine the biodiesel blend in mixtures and to find out the adulteration of oil in mixtures simultaneously with a simplified calibration modeling method. The researcher will introduce the work about monitoring the transesterification reaction process, while the other two issues will be introduced in the following sections. A TENSOR 27 FTIR spectrometer equipped with an Attenuated Total Reflectance (ATR) sampling accessory MIRacle ATR was used to get the ATR-FTIR spectra. The IR spectra of region of 1425–1447 $cm^{-1}$ and region of 1188–1200 $cm^{-1}$, where a slight difference in the spectra of oil and biodiesel was found, were used to develop the calibration model for quantification of the biodiesel concentration in the mixtures of soybean oil and biodiesel. Then the model was used to monitor the transesterification process. A good match between the predicated value of biodiesel composition and the actual value was found and the RMSEP was found to be 0.1246 which meant FTIR performed quite well. The author has concluded that both near-IR and mid-IR have been used for monitoring the transesterification reaction, however mid-IR has provided richer information.

### 3.3. Determination of biodiesel blend level

In recent years, biodiesel has gained international attention due to its importance as a renewable energy source. Biodiesel is free of sulphur and aromatic compounds and has a high cetane value [36]. However, it has higher viscosity, density, flash point, and lower cold-filter plugging point in relation to conventional mineral-based diesel [37]. Biodiesel is commonly used by blending with conventional petroleum-derived diesel fuel [38]. The amount of biodiesel in mixtures varies between 2 and 35 wt% in different countries; for example 5 and 30 wt% in France [39], 20 wt% in the USA and Canada [40], 30 wt% in the Czech and Slovak Republic [41]. It is necessary to determine the blend level of biodiesel rapidly and easily to make sure the fuel used indeed conforms to regulations, standards, and expected blend levels. Spectroscopic methods can be used for quantification if appropriate components in the mixture exhibit unique peaks that separated from those of other components.

As it was shown in many reports, IR is commonly used for this purpose. The first report was represented by Knothe [28] in which the fiber-optic near-IR spectroscopy was used to determine the blend level of biodiesel in conventional DF. The near-IR region was selected because the spectra display differences at 6005 $cm^{-1}$ and 4600–4800 $cm^{-1}$; which permitted a determination of the blend level of biodiesel blends with conventional diesel fuel. The well known carbonyl peak 1740–1750 $cm^{-1}$ in the mid-IR region was not used because the carbonyl peaks were virtually identical for vegetable oils and their methyl esters; as both contain the carbonyl functionality in ester form. Thus from the carbonyl absorption, it may not be possible to distinguish whether conventional DF was blended with methyl esters (biodiesel) or vegetable oil feedstock. The method presented was not precise for detecting low amounts of esters.

If the methyl esters are the only fraction within an ester functional group, the carbonyl peak in the mid-IR region would be a better choice to determine the biodiesel content. The valence vibration of the carbonyl group, between 1720 and 1760 $cm^{-1}$, was successfully used to determine the ME fraction in mixed fuels

by Bírová et al. [38], the carbonyl acid group in 1744 $cm^{-1}$ was used by Gołębiowski [42] to find out the RME concentration in biodiesel, and the C=O bond stretch at 1746 $cm^{-1}$ in the FTIR spectra was used for the quantification of biodiesel blends by Chuck et al. [43]. In their work, the total amount of MEs was determined by using the measurement of the carbonyl band intensity in the spectra of mixed fuel by FTIR. The results indicated that mid-IR was suitable to determine the ME fraction in mixed fuels. In Ref. [25], two other techniques, refractive index and UV–vis spectroscopy, were studied for gaining further information on the fatty acid profile of the biodiesel within the blend. Similar research work was also reported by Aliske et al. [44]. They pointed out that the mid-IR range was useful, since in this range there were many unmatched peaks between biodiesel and diesel oil including the carbonyl peak. Thus, mid-IR was adopted for measuring the biodiesel concentration in diesel oil that covers the full range of mixtures (0–100%). The carbonyl absorption peak, typical of esters, over the range from 1700 $cm^{-1}$ to 1800 $cm^{-1}$ was selected because the peak was present only in biodiesel, which made it a strong candidate for biodiesel–diesel oil mixture measurements. The mid-IR range is a much more sensitive range which made it possible to measure mixture percentiles of biodiesel in diesel oil, even at very low concentrations. Mid-IR was also used by Mahamuni and Adewuyi for biodiesel blend determination as stated before [35]. In the mid-IR spectrum, many differences were found in the spectra of biodiesel and petrodiesel, such as the large difference in the peak arrangement between the regions of 1700–1800 $cm^{-1}$ and 1000–1300 $cm^{-1}$ and others. However, only the region 1427–1472 $cm^{-1}$ was selected for biodiesel quantification in the blends, because in this region the differences between biodiesel, petro-diesel, and oil were found. Thus, the presence of small amounts of oil could not interfere with biodiesel analysis. The developed calibration model with EFCM software worked very well in predicting the actual values and the average error was below 0.1194.

Meanwhile, near-IR was preferred in predicting the biodiesel concentration by other researchers. In reference [45], Coronada reported his research work on predicting the biodiesel concentration of biodiesel and diesel blends with near-IR. Different biodiesels were used to prepare the samples which can represent the general type of biodiesel. It is well known that the range of 2100 to 2200 nm is assigned to straight carbon chains, and *cis*- double bonds that reflect fatty acid moieties in fat molecules. During the experiment the different absorbance value of different biodiesel blend levels were found. Thus, three best wavelengths were selected from the wavelength range of 2080 to 2200 nm to develop the calibration model with the multiple linear regression (MLR) method. The final average RMSEP of biodiesel concentration in the blends is 2.9% which means Near-IR was suitable for the prediction of biodiesel concentration. In reference [14], FT-NIR was used for classifying and quantifying the FA composition and in reference [37] FT-NIR was used together with multivariate control charts to monitor the biodiesel blend. Three kinds of charts were established based on the near infrared spectrum over the range from 5300 to 5740 $cm^{-1}$ and with which the concentration of biodiesel, diesel, soybean oil, and naphtha contaminated in the sample could be analyzed qualitatively. All of the research indicated that near-IR as well as mid-IR was a useful tool with great potential to provide the needed biodiesel concentration. This conclusion was confirmed by additional reported research in which both near-IR and mid-IR were used to determine the biodiesel concentration. Fernanda Pimentel [46] reported mid and near infrared spectroscopy were used to determine the content of biodiesel in diesel fuel blends. The determination considered the presence of raw vegetable oil and thus the multivariate calibration method was used to solve the problem of IR spectra overlapping because of the similarities of the vegetable oils and their respective esters. Together with PCA and PLS, the multivariable calibration models based on mid-IR and near-IR spectra were developed. For mid-IR the carbonyl group region 1700–1800 $cm^{-1}$ was selected and for near-IR the region from 2200 to 2280 nm was used. The models were proven suitable as a practical analytical method to predict biodiesel content in conventional diesel blends in the range of 0–5%, considering the possible presence of raw oil as a contaminant. Also in reference [47], the calibration models based on FT-NIR (transflectance-fiber optics) and ATR-FTIR combined with PLS and artificial neural network (ANN) analysis to determine the methyl ester contents in biodiesel blends (methyl ester+diesel) was developed. FT-NIR spectra were recorded using an immersion transflectance accessory coupled to a Ge detector by an optical fiber. The ATR-FTIR spectra were recorded using a 7 cm long horizontal ATR cell, using a DTGS detector. Suitable ranges were selected with the $\Psi\sigma_A/A\%$ method and the established calibration model proved to be precise and accurate in determining the biodiesel content in the mixture blends.

### *3.4. Analysis of biodiesel properties*

The properties of biodiesel such as density, viscosity, flash point, etc have great effects on the application of biodiesel. These important properties were prescribed in the European Standard (EN 14214) and the United States Standard (ASTM D 6751). The analytical methods that should be used to determine those properties were provided too, but these standard methods for assessing the quality of biodiesel are generally slow, time-consuming, and require high-cost specified equipment [5]. IR technology, as a promising alternative analytical method, has been found to be used in properties analyzing at a low cost, less time consuming, and nondestructive way. The researcher can determine that both FTIR and FT-NIR together with PLS and artificial network methods have been successfully used in diesel property analysis. From Ref. [48], the properties including density, viscosity, and cetane index were determined with the established calibration models. Some research works reported recently have shown the viability of both near-IR and mid-IR spectroscopy associated with multivariate calibration to estimate the properties of biodiesel.

The first property for biodiesel analysis is the ester content. Knothe pointed out the ester content was very important because the overall fuel properties of the biodiesel were determined by the properties of the various individual fatty esters that comprise biodiesel. The properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester [49]. Baptista et al. [15] thought the ester content was one of the first properties, if not the first, to be measured to assess the quality of biodiesel. During the researcher's work, it was found that IR technology was a better choice to be used to analyze the ester content. In the research work of Baptista et al. [15], near-IR spectroscopy combined with multivariate calibration was used to determine the esters content in biodiesel, as well as the linolenic acid methyl esters (C18:3) content in industrial and laboratory-scale biodiesel samples. The samples were prepared carefully to ensure the ester contents cover the whole ranges. PCA and PLS were used for the qualitative analysis of the spectra and the establishment of calibration models within the region from 4500 to 9000 $cm^{-1}$. For the linolenic acid methyl ester content, the error obtained (0.18%) was more than three times lower than the error mentioned in EN14103. Later, another achievement in determining important biodiesel properties such as the iodine value, the cold filter plugging point, the kinematic viscosity at 40 °C and the density

at 15 °C with near-IR was reported by the same research group in Ref. [50]. PCA was used to perform a qualitative analysis of the spectra and partial least squares regression was used to develop the calibration models between analytical and spectral data. The results support that near-IR spectroscopy, in combination with multivariate calibration, is a promising technique applied to biodiesel quality control, in both laboratory and industrial-scale samples.

Mid-IR was also used in biodiesel property analysis. In Tseng's research work [51], an internet enabled quality trait analysis FTIR system was developed to analyze the properties of biodiesel. The system was comprised of a FTIR spectrometer, a temperature controlled ATR sampling device, a computer connected to both the FTIR spectrometer and internet, and a powerful server with the capability of data treatment, model prediction, data storage, and data distribution. With this system, a set of biodiesel properties such as acid value tri-, di-, and monoglycerides were achieved successfully in less than 2 min. FTIR was also preferred by Lima et al. [52], as in his research work a FTIR spectroscopic spectrophotometer combined with a photoacoustic detector was used for qualitative analysis of biodiesel. Through the difference between the spectra of unwashed and washed biodiesel and different glycerol contents can be obviously determined; FTIR can thus be used to contribute to the biodiesel wash process in order to separate the glycerol from the biodiesel. Another example using FTIR to analyze properties of biodiesel is found in the research of Younis et al. [53]. Different biodiesels are produced with different kinds of vegetable oil. Characterization of biodiesel was done through different experiments, using ASTM standards such as D97 for pour point, D189 for carbon residue, and D93 for flash point. Besides these standard tests, FTIR was also performed to test and explain these properties of biodiesel. The infrared spectrum of each sample was obtained in which the bond's concentrations within the sample were analyzed so that the properties of each biodiesel sample could be easily evaluated.

Several studies in the literature have also shown the use of both mid-IR and near-IR together with multivariate calibration to analyze the properties of biodiesel. The stability of biodiesel was analyzed by the analytical methods based on near-IR and mid-IR spectroscopy and multivariate calibration through three parameters: oxidative stability index, acid number, and water content in reference [54]. The samples were collected at intervals of 3–4 days from the biodiesel from different origins. A FTIR Perkin Elmer Spectrum GX spectrometer was used to obtain the near-IR (12,000 to 4000 $cm^{-1}$) and mid-IR (4000 to 600 $cm^{-1}$) spectra. The spectra were acquired using a quartz flow cell in the near-IR region and an ATR probe in the mid-IR region. PLS and MLR were adopted for multivariate calibration in which strategies for selection of spectral regions and variables were evaluated. The results indicated the use of IR spectroscopy to determine these three parameters could provide an economic and quick way to monitor the stability of biodiesel during storage. Similar analytical methods were used in analyzing the properties (density, sulphur content, and distillation temperatures) of biodiesel/diesel blends by De Fátima Bezerra de Lira et al. [55]. A common use of biodiesel is in blends with diesel fuel, so assessing the properties of biodiesel blends is very important. In this work, multivariate calibration models were developed employing near-IR and mid-IR spectra to predict important quality parameters of biodiesel blends (density, sulphur content, and distillation temperatures). The near-IR (12,000–4000 $cm^{-1}$) and mid-IR (4000–600 $cm^{-1}$) spectra were obtained with a FTIR Perkin-Elmer Spectrum GX spectrometer using a quartz flow cell and an ATR probe respectively. Mid-IR spectra (1789.4–650 $cm^{-1}$) were also obtained with a portable FTIR instrument from Grabner Instruments. Calibration models were established according to spectra obtained with PLS method and the performances of models were analyzed respectively. The results obtained from the evaluation by RMSEP demonstrated that calibration models employing near-IR and mid-IR regions could be used to predict properties of biodiesel/diesel blends.

### 3.5. Contaminants analyzing of biodiesel

Biodiesel is a renewable fuel obtained by a transesterification reaction, in which fatty acid reacts with methanol in the presence of alkali (the catalyst) and transformed into the corresponding FAME with concurrent production of glycerol. The resulting FAME mixture termed 'biodiesel' is easily contaminated with mono-, di-, and triglycerides, methanol, free glycerol, catalyst, soap, and water. Meanwhile, the insoluble material was found sometimes in finished biodiesel after a period of storage, particularly at low temperature, or when the biodiesel was exposed to high temperatures in the presence of oxygen. All these contaminants may affect the quality and performance of biodiesel which may cause severe engine problems. Thus, contaminant analysis is an important aspect of biodiesel quality control. Standards are established to limit the amount of contaminants in biodiesel. Known from many literatures reported, the IR technique has played an important role in contaminant analysis within biodiesel.

In reference [56], Bondioli reported a white insoluble product which is sometimes present in finished biodiesel samples, mainly prepared using palm or soybean oil as a feedstock. FTIR was used to identify this contaminant after the solid was isolated and purified. Infrared spectra were recorded, the strong absorptions of the spectrum present the needed information, and the solid was identified as a mixture of phytosteryl glucosides. Similar research work was reported in his paper [57]. FTIR technique was used to provide some preliminary information about the nature of the isolated and purified solid product recovered from the biodiesel samples. The similar use of FTIR in the research work of Tang et al. [58] should be observed as different biodiesel blends were studied after storage at 4 °C and precipitates were observed. FTIR together with GC-FID were used to identify the nature of the precipitate. The FTIR spectra of the precipitates formed by different biodiesel blends were compared with standard steryl glucoside, and the absorption peaks in the spectra of precipitates coincided with the standard steryl glucoside, which meant the precipitates were mainly due to steryl glucosides.

The problem of contaminants in biodiesel was also studied by other researchers concerning IR technique. Felizardo reported his research determining the content of water and methanol in industrial and laboratory scale biodiesel samples with near-IR in his two published papers [59,60]. In Felizardo's work, near-IR spectroscopy was used to develop the calibration models to relate the near infrared spectrum of biodiesel with the analytical data. The near-IR diffuse transflectance spectra of the biodiesel samples were acquired using an ABB Bomem MB160 spectrometer equipped with an InGaAs detector and a transflectance probe. It was found that the O–H group of water presented a peak at 5200 $cm^{-1}$, the hydroxyl group of methanol showed a relatively broad peak at 4885–4480 $cm^{-1}$ [29,61,62]. Thus after excluding the noisy and non-informative ranges of the spectra, the regions between 4500 and 9000 $cm^{-1}$, 5000–6200 $cm^{-1}$, and 5100–5400 $cm^{-1}$ were selected for calibration of water content. The region between 4500 and 9000 $cm^{-1}$ was used for methanol calibration, meanwhile a narrow spectral region where methanol displays its typical signal (4800–5050 $cm^{-1}$) was selected just for verification purposes. PCA and PLS were used during the multivariate calibration. The results obtained indicated that the established models all had a good predictive ability and the use of a larger spectral region for calibration still can get good results. The

values of RMSEP were similar to the ones presented in the European Standard for the reference methods. Thus, the near-IR spectroscopy was proved to be a promising tool to determine the amount of water and methanol in biodiesels.

Another problem in biodiesel quality control is to eliminate the fuel adulteration or in other words, vegetable oils are added in the biodiesel. Adulteration of biodiesel with vegetable oils is a common situation of biodiesel contamination. It is worth mentioning that this kind of contamination can lead to social, economical, and environmental problems such as loss on incoming taxes, damage to the diesel engine, and an increase in particulate emission due to the incomplete combustion. The use of raw vegetable oils directly into engines can cause carbon deposits, blocking of injectors, and incomplete combustion because of their high viscosities, low volatilities, and polyunsaturated character, as well as its gum formation characteristic due to oxidation and polymerization [63]. Thus, it is important to develop a methodology that can be used quickly, easily, and economically to get information about whether or not the biodiesel was adulterated with raw vegetable oils. From the research work reported, it was found that IR spectroscopy had been used successfully in this kind of analyzing work. Oliveira et al. [64] reported that vibration spectroscopy (Fourier transform near infrared spectrometry and FT-Raman) was used to identify adulterations of B2 and B5 blends with vegetable oils. The calibration models based on multivariate analysis such as principal component regression (PCR), and PLS as well as ANN, were developed to quantify the presence of vegetable oils in biodiesel blends (B2 and B5). According to the author, the PCR and PLS/FTNIR calibration models are able to determine the adulteration of diesel/biodiesel blends with vegetable oils with an accuracy greater than 0.05% (w/w).

Also, the use of mid-IR was found in solving this kind of problem. Soares has reported his research work on detecting this kind of adulteration in a fast, precise, and accurate way with FTIR in two papers [65,66]. In the work reported in reference [65], ATR-FTIR spectra data of biodiesel samples from different sources, such as cotton, castor, and palm were used to develop a calibration model with PLS calibration method for quantification of the amount of raw soybean oil mixed in the biodiesel from 1 to 40% (v/v). According to the author, the calibration model based on mid-IR developed in this study seems to be quite good because it could preview with 95% of significance from all samples analyzed. Different variable selection methods were used and compared during the application. In reference [66], the physical chemistry properties changes of biodiesel B2 adulterated with residual oil were studied and a calibration model was built with PLS multivariate calibration method and was applied to ATR-FTIR data to quantify the residual oil present in each sample. The ATR-FTIR technique was shown to be very efficient in the determination of adulteration of B2 with residual oil from 0.5 to 25% (w/w). In summary, both near-IR and mid-IR can be used to detect the adulteration of vegetable oil in biodiesel, therefore it was no surprise to find that near-IR and mid-IR were used simultaneously for detecting the adulteration of vegetable oil in diesel/biodiesel blends by Gaydou et al. [67]. FT-NIR spectra between 4430 and 10,000 $cm^{-1}$ and FT-MIR spectra between 650 and 4000 $cm^{-1}$ were recorded separately, and three multiblocks method, concatenated method, Hierarchical-PLS (H-PLS), and Serial-PLS (S-PLS) were chosen to establish the calibration models. Concatenated method consists in concatenating the descriptor block into the same matrix and then applying PLS regression. H-PLS consists in considering each block independently at the beginning with PCA and then the scores obtained in each block were collected together to form a super matrix. The PLS regression was then applied on the super matrix. As for S-PLS, the PLS regression was applied on each block and then the scores obtained in each block are collected together to form a super matrix. The PLS regression was then applied on the super matrix. The models obtained were compared in term of prediction errors (RMSEP). The multiblocks methodology seems to be of great interest in quantitative analysis with the simultaneous use of information from the mid-IR and near-IR spectroscopy.

## 4. Conclusion

There can be little doubt that IR techniques including near-IR and mid-IR have demonstrated considerable potential for biodiesel quality analysis by providing a rapid, low cost, and highly reproducible analyzing tool. Almost all the issues related to biodiesel analysis were found to be resolved successfully with IR techniques. Ready transfer of this technique to the analytical application of biodiesel is already possible. It is worth mentioning that there is no feasible, ideal method for all purposes. Both near-IR and mid-IR have their own advantages and disadvantages and which one is a better choice is dependent on the specific analysis requirements. In general, mid-IR has made a huge contribution in providing the structure information of functional groups in the sample. Near-IR has played a role in quantitative analysis of compounds that contain functional groups with hydrogen together with carbons, nitrogen, and oxygen. Near-IR and mid-IR can be used separately or together in biodiesel analyzing work, while further research work is needed to determine whether the combined information produces better or worse predictions in biodiesel analysis. Multivariate analysis and chemometrics are necessary during qualitative and quantitative analyzing work of biodiesel, and the results illustrated in this review showed that IR techniques together with appropriate multivariate methods and chemometric tools enabled a better control and analysis of biodiesel according to their potential abilities. Indeed, with the ever increasing power of personal computers and measuring instruments, the IR technique will be more extensively applied in the area of biodiesel analysis in the future.

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## References

[1] Srivastava A, Prasad R. Triglycerides-based diesel fuels. Renewable and Sustainable Energy Reviews 2000;4(2):111–33.
[2] Demirbas A. Progress and recent trends in biodiesel fuels. Energy Conversion and Management 2009;50(1):14–34.
[3] Knothe G, Matheaus C, Thomas W. Cetane numbers of branched and straightchain fatty esters determined in an ignition quality tester. Fuel 2003;82(8):971–5.
[4] Hernando J, Leton MP, Novella J, Builla A. Biodiesel and FAME synthesis assisted by microwaves: homogenous batch and flow processes. Fuel 2007;86(10–11):1641–4.
[5] Knothe G. Analyzing biodiesel: standards and other methods. Journal of the American Oil Chemists' Society 2006;83(10):823–33.
[6] Knothe G. Analytical methods used in the production and fuel quality assessment of biodiesel. Transactions of the ASAE 2001;44(2):193–200.
[7] Monteiro MR, Ambrozin ARP, Lião LM, Ferreira AG. Critical review on analytical methods for biodiesel characterization. Talanta 2008;77(2):593–605.

[8] Skoog DA, Holler FJ, Nieman TA. Principles of instrumental analysis. 4th ed.Saunders College Publishing; 1992.

[9] Lin M, Al-Holy M, Al-Qadiri H, Kang D-H, Cavinato AG, Huang Y, et al. Discrimination of intact and injured *Listeria monocytogenes* by Fourier Transform Infrared Spectroscopy and Principal Component Analysis. Journal of Agricultural and Food Chemistry 2004;52(19):5769–72.

[10] Xixiong Z, Jun L, Zhihong W, Zhiyu W. The application of chemometric methods in near infrared spectroscopy analysis. In: 2nd IEEE conference on industry electronics and applications. Harbin; 2007. p. 1771–4.

[11] Özdemir D, Öztürk B. Near infrared spectroscopic determination of olive oil adulteration with sunflower and corn oil. Journal of Food and Drug Analysis 2007;15(1):40–7.

[12] Font R, Celstino M, Bailón A. The use of near-infrared spectroscopy (NIRS) in the study of seed quality components in plant breeding programs. Industrial Crops and Products 2006;24(3):307–13.

[13] McKelvy ML, Britt TR, Davis BL, Gillie JK, Graves FB, Lentz LA. Infrared spectroscopy. Analytical Chemistry 1998;70(12):119–77.

[14] Aziziana H, Kramer JKG. A rapid method for the quantification of fatty acids in fats and oils with emphasis on *trans* fatty acids using Fourier Transform Near Infrared Spectroscopy (FT-NIR). Lipids 2005;40(8):855–67.

[15] Baptista P, Felizardo P, Menezes JC, Correia MJN. Multivariate near infrared spectroscopy models for predicting the methyl esters content in biodiesel. Analytica Chimica Acta 2008;607(2):153–9.

[16] Özgül-Yücel S, Proctor A. Rice bran F.F.A. determination by diffuse reflectance IR spectroscopy. Journal of the American Oil Chemists' Society 2004;81(3): 221–4.

[17] Aryee ANA, van de Voort FR, Simpson BK. FTIR determination of free fatty acids in fish oils intended for biodiesel production. Process Biochemistry 2009;44(4):401–5.

[18] Li Y, García-González DL, Yu X, van de Voort FR. Determination of free fatty acids in edible oils with the use of a variable filter array IR spectrometer. Journal of the American Oil Chemists' Society 2008;85(7):599–604.

[19] Moser BR, Knothe G, Vaughn SF, Isbell TA. Production and evaluation of biodiesel from field pennycress (*Thlaspi arWense* L.) oil. Energy & Fuels 2009;23(8): 4149–55.

[20] Jham GN, Moser BR, Shah SN, Holser RA, Dhingra OD, Vaughn SF, et al. Wild Brazilian mustard (*Brassica juncea* L.) seed oil methyl esters as biodiesel fuel. Journal of the American Oil Chemists' Society 2009;86(9):917–26.

[21] Sarin R, Sharma M, Khan AA. Studies on *Guizotia abyssinica* L. oil: biodiesel synthesis and process optimization. Bioresource Technology 2009;100(18): 4187–92.

[22] Shang Q, Jiang W, Lu H, Liang B. Properties of Tung oil biodiesel and its blends with 0# diesel. Bioresource Technology 2010;101(2):826–8.

[23] Qin S, Sun Y, Meng X, Zhang S. Production and analysis of biodiesel from non-edible seed oil of *Pistacia chinensis*. Energy, Exploration & Exploitation 2010;28(1):37–46.

[24] Branco PC, Castilho PC, Rosa MF, Ferreira J. Characterization of annona cherimola mill. Seed oil from Madeira island: a possible biodiesel feedstock. Journal of the American Oil Chemists' Society 2010;87(4):429–36.

[25] Kleinová A, Cvengroš J. Utilization of used frying oils/fats in FAME production. In: 44th international petroleum conference. Bratislava, Slovak Republic; 2009. p. 21–2.

[26] Innawong B, Mallikarjunan P, Irudayaraj J, Marcy JE. The determination of frying oil quality using Fourier transform infrared attenuated total reflectance. LWT—Food Science and Technology 2004;37(1):23–8.

[27] Baptista P, Felizardo P, Menezes J, Neiva CM. Monitoring the quality of oils for biodiesel production using multivariate near infrared spectroscopy models. Journal of Near Infrared Spectroscopy 2008;16(5):445–54.

[28] Knothe G. Determining the blend level of mixtures of biodiesel with conventional diesel fuel by fiber-optic near-infrared spectroscopy and 1H nuclear magnetic resonance spectroscopy. Journal of the American Oil Chemists' Society 2001;78(10):1025–8.

[29] Knothe G. Rapid monitoring of transesterification and assessing biodiesel fuel quality by near-infrared spectroscopy using a fiber-optic probe. Journal of the American Oil Chemists' Society 1999;76(7):795–800.

[30] Knothe G. Monitoring a progressing transesterification reaction by fiber-optic near infrared spectroscopy with correlation to 1H nuclear magnetic resonance spectroscopy. Journal of the American Oil Chemists' Society 2000;77(5): 489–93.

[31] Dubé MA, Zheng S, McLean DD, Kates MA. Comparison of attenuated total reflectance-FTIR spectroscopy and GPC for monitoring biodiesel production. Journal of the American Oil Chemists' Society 2004;81(6):599–603.

[32] Zagonel GF, Peralta-Zamora P, Ramos LP. Multivariate monitoring of soybean oil ethanolysis by FTIR. Talanta 2004;63(4):1021–5.

[33] Siatis NG, Kimbaris AC, Pappas CS, Tarantilis PA, Polissiou MG. Improvement of biodiesel production based on the application of ultrasound: monitoring of the procedure by FTIR spectroscopy. Journal of the American Oil Chemists' Society 2006;83(1):53–7.

[34] Trevisan MG, Garcia CM, Schuchardt U, Poppi RJ. Evolving factor analysis—based method for correcting monitoring delay in different batch runs for use with PLS: on-line monitoring of a transesterification reaction by ATR-FTIR. Talanta 2008;74(4):971–6.

[35] Mahamuni NN, Adewuyi YG. Fourier transform infrared spectroscopy (FTIR) method to monitor soy biodiesel and soybean oil in transesterification reactions, petrodiesel-biodiesel blends, and blend adulteration with soy oil. Energy & Fuels 2009;23(7):3773–82.

[36] Knothe G, Steidley KR. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel 2005;84(9):1059–65.

[37] De Oliveira IK, de Carvalho Rocha WF, Poppi RJ. Application of near infrared spectroscopy and multivariate control charts for monitoring biodiesel blends. Analytica Chimica Acta 2009;642(1–2):217–21.

[38] Bírová A, Švajdlenka E, Cvengros J, Dostálíková V. Determination of the mass fraction of methyl esters in mixed fuels. European Journal of Lipid Science and Technology 2002;104(5):271–7.

[39] Sabin JC. Rape ester: a key factor for rural development. In: Proceedings of the 1st European forum on motor biofuels. Tours, France; 1994. p. 30–1.

[40] Körbitz W. Biodiesel development status world-wide 1997. In: Proceedings of the 1998 PORIM international biofuel and lubricant conference. Kuala Lumpur, Malaysia; 1998. p. 3–22.

[41] Pokorný Z, Cvengroš J. Biodiesel and bioetanol in Czech Republic and Slovak Republic—present state, production prospectives and utilization. In: Proceedings of the 10th Europe conference and technology exhibition. Würzburg, Germany; 1998. p. 549–51.

[42] Gołębiowski J. The analysis of the rapeseed methyl ester absorption spectra applied to the determination of biodiesel composition. 〈http://www.wseas.us/e-library/conferences/izmir2004/papers/489-390.pdf〉 [website accessed June 2011].

[43] Chuck CJ, Bannister CD, Gary Hawley J, Davidson MG. Spectroscopic sensor techniques applicable to real-time biodiesel determination. Fuel 2010;89(2): 457–61.

[44] Aliske MA, Zagonel GF, Costa BJ, Veiga W, Saul CK. Measurement of biodiesel concentration in a diesel oil mixture. Fuel 2007;86(10–11):1461–4.

[45] Coronado M, Yuan W, Wang D, Dowell FE. Predicting the concentration and specific gravity of biodiesel–diesel blends using near-infrared spectroscopy. Applied Engineering in Agriculture 2009;25(2):217–21.

[46] Fernanda Pimentel M, Ribeiro GMGS, da Cruz RS, Stragevitch L, Pacheco Filho JGA, Teixeira LSG. Determination of biodiesel content when blended with mineral diesel fuel using infrared spectroscopy and multivariate calibration. Microchemical Journal 2006;82(2):201–6.

[47] Oliveira JS, Montalvão R, Daher L, Suarez PAZ, Rubim JC. Determination of methyl ester contents in biodiesel blends by FTIR-ATR and FTNIR spectroscopies. Talanta 2006;69(5):1278–84.

[48] Santos Jr. VO, Oliveira FCC, Lima DG, Petry AC, Rubim JC. A comparative study of diesel analysis by FTIR, FTNIR and FT-Raman spectroscopy using PLS and artificial neural network analysis. Analytica Chimica Acta 2005;547(2): 188–96.

[49] Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Processing Technology 2005;86(10):1059–70.

[50] Baptista P, Felizardo P, Menezes JC, Correia MJN. Multivariate near infrared spectroscopy models for predicting the iodine value, CFPP, kinematic viscosity at 40 °C and density at 15 °C of biodiesel. Talanta 2008;77(1): 144–51.

[51] Tseng C-H, Wang N. Fast analysis of fats, oils and biodiesel by FT-IR. Lipid Technology 2007;19(2):39–40.

[52] Lima SM, Izida1 T, Figueiredo MS, Andrade LHC, Del RPV, Jorge N, et al. Analysis of biodiesel and frying vegetable oils by means of FTIR photoacoustic spectroscopy. The European Physical Journal—Special Topics 2008;153(1): 535–7.

[53] Younis MN, Saeed MS, Khan S, Furqan MU, Khan RU, Saleem M. Production and characterization of biodiesel from waste and vegetable oils. Journal of Quality and Technology Management 2009;1:111–21.

[54] De Lira LFB, de Albuquerque MS, Pacheco JGA, Fonseca TM, de Siqueira EH, Stragevitch L, et al. Infrared spectroscopy and multivariate calibration to monitor stability quality parameters of biodiesel. Microchemical Journal 2010;96(1):126–31.

[55] De Fátima Bezerra de Lira L, de Vasconcelos FVC, Pereira CF, Pimentel MF. Prediction of properties of diesel/biodiesel blends by infrared spectroscopy and multivariate calibration. Fuel 2010;89(2):405–9.

[56] Bondioli P, Cortesi N, Mariani C. Identification and quantification of steryl glucosides in biodiesel. European Journal of Lipid Science and Technology 2008;110(2):120–6.

[57] Bondioli P. Nature of some insoluble materials recovered from biodiesel samples. European Journal of Lipid Science and Technology 2009;111(8): 814–21.

[58] Tang H, Salley SO, Simon Ng KY. Fuel properties and precipitate formation at low temperature in soy-, cottonseed-, and poultry fat-based biodiesel blends. Fuel 2008;87(13–14):3006–17.

[59] Felizardo P, Baptista P, Uva MS, Menezes JC, Correia MJN. Monitoring biodiesel fuel quality by near infrared spectroscopy. Journal of Near Infrared Spectroscopy 2007;15(2):97–105.

[60] Felizardo P, Baptista P, Menezes JC, Correia MJN. Multivariate near infrared spectroscopy models for predicting methanol and water content in biodiesel. Analytica Chimica Acta 2007;595(1–2):107–13.

[61] Takamura H, Endo N, Matoba T. Near infrared spectroscopic determination of moisture content in foods: extraction method by organic solvents. Journal of Near Infrared Spectroscopy 1998;6:235–40.

[62] Li Y, Brown CW, Lo SC. Near infrared spectroscopic determination of alcohols—solving non-linearity with linear and nonlinear methods. Journal of Near Infrared Spectroscopy 1999;7:55–62.

[63] Leung DYC, Koo BCP, Guo Y. Degradation of biodiesel under different storage conditions. Bioresource Technology 2006;97(2):250–6.

[64] Oliveira FCC, Brandao CRR, Ramalho HF, da Costa LAF, Suarez PAZ, Rubim JC. Adulteration of diesel/biodiesel blends by vegetable oil as determined by Fourier transform (FT) near infrared spectrometry and FT-Raman spectroscopy. Analytica Chimica Acta 2007;587(2):194–9.
[65] Soares IP, Rezende TF, Silva RC, Castro EVR, Fortes ICP. Multivariate calibration by variable selection for blends of raw soybean oil/biodiesel from different sources using fourier transform infrared spectroscopy (FTIR) spectra data. Energy & Fuels 2008;22(3):2079–83.
[66] Soares IP, Rezende TF, Fortes ICP. Study of the behavior changes in physical-chemistry properties of diesel/biodiesel (B2) mixtures with residual oil and its quantification by partial least-squares attenuated total reflection-fourier transformed infrared spectroscopy (PLS/ATR-FTIR). Energy & Fuels 2009;23(8):4143–8.
[67] Gaydou V, Kister J, Dupuy N. Evaluation of multiblock NIR/MIR PLS predictive models to detect adulteration of diesel/biodiesel blends by vegetal oil. Chemometrics and Intelligent Laboratory Systems 2011;106(2):190–7.